

FORM PTO-1390  
(REV. 11-2000)

U.S. DEPARTMENT OF COMMERCE PATENT AND TRADEMARK OFFICE

ATTORNEY'S DOCKET NUMBER

TRANSMITTAL LETTER TO THE UNITED STATES  
DESIGNATED/ELECTED OFFICE (DO/EO/US)  
CONCERNING A FILING UNDER 35 U.S.C. 371

Mo-6368/Lea 33,233

U.S. APPLICATION NO. (If known, see 37 CFR 1.5)

09/868211

To be Assigned

INTERNATIONAL APPLICATION NO.

INTERNATIONAL FILING DATE

PRIORITY DATE CLAIMED

PCT/EP99/09527

06 December 1999 (6.12.99)

18 December 1998 (18.12.98)

TITLE OF INVENTION WOOL WITH ANTIFELT FINISH AND METHOD FOR PROVIDING AN ANTIFELT FINISH

APPLICANT(S) FOR DO/EO/US 1) Bernhard Jansen; 2) Ferdinand Kummeler

Applicant herewith submits to the United States Designated/Elected Office (DO/EO/US) the following items and other information:

1. ☒ This is a **FIRST** submission of items concerning a filing under 35 U.S.C. 371.
2. ☐ This is a **SECOND** or **SUBSEQUENT** submission of items concerning a filing under 35 U.S.C. 371.
3. ☒ This is an express request to begin national examination procedures (35 U.S.C. 371(f)). The submission must include items (5), (6), (9) and (21) indicated below.
4. ☒ The US has been elected by the expiration of 19 months from the priority date (Article 31).
5. ☒ A copy of the International Application as filed (35 U.S.C. 371(c)(2))
  - a. ☒ is attached hereto (required only if not communicated by the International Bureau).
  - b. ☐ has been communicated by the International Bureau.
  - c. ☐ is not required, as the application was filed in the United States Receiving Office (RO/US).
6. ☒ An English language translation of the International Application as filed (35 U.S.C. 371(c)(2)).
  - a. ☒ is attached hereto.
  - b. ☐ has been previously submitted under 35 U.S.C. 154(d)(4).
7. ☐ Amendments to the claims of the International Application under PCT Article 19 (35 U.S.C. 371(c)(3))
  - a. ☐ are attached hereto (required only if not communicated by the International Bureau).
  - b. ☐ have been communicated by the International Bureau.
  - c. ☐ have not been made; however, the time limit for making such amendments has NOT expired.
  - d. ☐ have not been made and will not be made.
8. ☐ An English language translation of the amendments to the claims under PCT Article 19 (35 U.S.C. 371 (c)(3)).
9. ☒ An oath or declaration of the inventor(s) (35 U.S.C. 371(c)(4)).
10. ☐ An English language translation of the annexes of the International Preliminary Examination Report under PCT Article 36 (35 U.S.C. 371(c)(5)).

## Items 11 to 20 below concern document(s) or information included:

11. ☐ An Information Disclosure Statement under 37 CFR 1.97 and 1.98.
12. ☒ An assignment document for recording. A separate cover sheet in compliance with 37 CFR 3.28 and 3.31 is included.
13. ☒ A FIRST preliminary amendment.
14. ☐ A SECOND or SUBSEQUENT preliminary amendment.
15. ☐ A substitute specification.
16. ☐ A change of power of attorney and/or address letter.
17. ☐ A computer-readable form of the sequence listing in accordance with PCT Rule 13ter.2 and 35 U.S.C. 1.821 - 1.825.
18. ☒ A second copy of the published international application under 35 U.S.C. 154(d)(4).
19. ☐ A second copy of the English language translation of the international application under 35 U.S.C. 154(d)(4).
20. ☒ Other items or information:

PTO Form 1449 and references listed therein; Preliminary Amendment w/Abstract

U.S. APPLICATION NO. (known, (37 CFR 1.51))  
To be assigned **09/868211**INTERNATIONAL APPLICATION NO  
PCT/EP99/09527ATTORNEY'S DOCKET NUMBER  
Mo-6368/LeA 33,233

21. <input checked="" type="checkbox"/> The following fees are submitted:				CALCULATIONS PTO USE ONLY	
<b>BASIC NATIONAL FEE (37 CFR 1.492 (a) (1) - (5)):</b> Neither international preliminary examination fee (37 CFR 1.482) nor international search fee (37 CFR 1.445(a) (2)) paid to USPTO and International Search Report not prepared by the EPO or JPO ..... \$1000.00  International preliminary examination fee (37 CFR 1.482) not paid to USPTO but International Search Report prepared by the EPO or JPO ..... \$860.00  International preliminary examination fee (37 CFR 1.482) not paid to USPTO but international search fee (37 CFR 1.445(a)(2)) paid to USPTO ..... \$710.00  International preliminary examination fee (37 CFR 1.482) paid to USPTO but all claims did not satisfy provisions of PCT Article 33(1)-(4) ..... \$690.00  International preliminary examination fee (37 CFR 1.482) paid to USPTO and all claims satisfied provisions of PCT Article 33(1)-(4) ..... \$100.00  <b>ENTER APPROPRIATE BASIC FEE AMOUNT =</b>				\$	860.00
Surcharge of \$130.00 for furnishing the oath or declaration later than <input type="checkbox"/> 20 <input type="checkbox"/> 30 months from the earliest claimed priority date (37 CFR 1.492(e)).				\$	
CLAIMS	NUMBER FILED	NUMBER EXTRA	RATE	\$	
Total claims	14 -20 =	0	x \$18.00	\$	0.00
Independent claims	2 -3 =	0	x \$80.00	\$	0.00
MULTIPLE DEPENDENT CLAIM(S) (if applicable)			+ \$270.00	\$	
<input checked="" type="checkbox"/> <b>TOTAL OF ABOVE CALCULATIONS =</b>				\$	860.00
<input type="checkbox"/> Applicant claims small entity status. See 37 CFR 1.27. The fees indicated above are reduced by 1/2.				\$	
<b>SUBTOTAL =</b>				\$	860.00
Processing fee of \$130.00 for furnishing the English translation later than <input type="checkbox"/> 20 <input type="checkbox"/> 30 months from the earliest claimed priority date (37 CFR 1.492(f)).				\$	
<b>TOTAL NATIONAL FEE =</b>				\$	860.00
Fee for recording the enclosed assignment (37 CFR 1.21(h)). The assignment must be accompanied by an appropriate cover sheet (37 CFR 3.28, 3.31). \$40.00 per property +				\$	40.00
<b>TOTAL FEES ENCLOSED =</b>				\$	900.00
				Amount to be refunded:	\$
				charged:	\$

- a. ☐ A check in the amount of \$ \_\_\_\_\_ to cover the above fees is enclosed.
- b. ☒ Please charge my Deposit Account No. 13-3848 in the amount of \$ 900.00 to cover the above fees.  
A duplicate copy of this sheet is enclosed.
- c. ☒ The Commissioner is hereby authorized to charge any additional fees which may be required, or credit any  
overpayment to Deposit Account No. 13-3848. A duplicate copy of this sheet is enclosed.
- d. ☐ Fees are to be charged to a credit card. **WARNING:** Information on this form may become public. Credit card  
information should not be included on this form. Provide credit card information and authorization on PTO-2038.

**NOTE:** Where an appropriate time limit under 37 CFR 1.494 or 1.495 has not been met, a petition to revive (37 CFR 1.137 (a) or (b)) must be filed and granted to restore the application to pending status.

SEND ALL CORRESPONDENCE TO:

Richard E.L. Henderson  
Bayer Corporation  
Patent Department  
100 Bayer Road  
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USA



**00157**  
PATENT TRADEMARK OFFICE

Richard E.L. Henderson  
SIGNATURE

Richard E.L. Henderson  
NAME

31,619  
REGISTRATION NUMBER

PATENT APPLICATION  
Mo-6368  
LeA 33,233

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

APPLICATION OF )  
BERNHARD JANSEN ET AL )  
SERIAL NUMBER: TO BE ASSIGNED )  
FILED: HEREWITH )  
TITLE: WOOL WITH ANTIFELT FINISH )  
AND METHOD FOR PROVIDING )  
AN ANTIFELT FINISH )

PRELIMINARY AMENDMENT

Assistant Commissioner for Patents

Washington, D.C. 20231

Sir:

Prior to examination, please amend the application as follows.

"Express Mail" mailing label number ET146886964US  
Date of Deposit June 14, 2001

I hereby certify that this paper or fee is being deposited with the United States Postal Service "Express Mail Post Office to Addressee" service under 37 CFR 1.10 on the date indicated above and is addressed to the Assistant Commissioner of Patents and Trademarks, Washington, D.C. 20231

Dorothy P. Colangelo  
(Name of person mailing paper or fee)  
Dorothy P. Colangelo  
(Signature of person mailing paper or fee)

IN THE SPECIFICATION:

Please replace the title at page 1, line 1, with

--WOOL WITH ANTIFELT FINISH AND  
METHOD FOR PROVIDING AN ANTIFELT FINISH--

IN THE CLAIMS:

Please replace the heading at page 20, line 1 with --WHAT IS CLAIMED IS:--

Please cancel Claims 1-13 and add Claims 14-27.

--14. A nonfelting wool obtained by a process comprising exposing wool to

- (a) a plasma in a pretreatment, followed by
- (b) optionally, an aqueous dispersion of self-dispersing isocyanates,
- (c) a softener, and
- (d) optionally, an antislip agent.

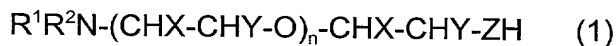
15. A nonfelting wool obtained by a process comprising exposing wool to

- (a) a plasma in a pretreatment, followed by
- (b) an aqueous dispersion of self-dispersing isocyanates,
- (c) a softener, and
- (d) optionally, an antislip agent.

16. A nonfelting wool according to Claim 14 wherein the wool is raw wool obtained after a raw wool scour, dyed or undyed wool slubbing, or a dyed or undyed wool yarn, knit, or cloth.

17. A nonfelting wool according to Claim 14 wherein the self-dispersing isocyanate has an isocyanate content of 1 to 25% by weight, reckoned as NCO (having a molecular weight of 42 g/mol), and is obtained by reaction in any order of

- (I) organic polyisocyanates having an average NCO functionality of 1.8 to 4.2 with
- (II) polyalkylene oxide alcohols, amines, and/or thiols of the formula (1)



wherein

n is 3 to 70,

X and Y are hydrogen or methyl, with the proviso that when one of X and Y is methyl the other of X and Y must be hydrogen,

R<sup>1</sup> and R<sup>2</sup> are independently straight-chain or branched C<sub>1</sub>-C<sub>6</sub>-alkyl radicals or straight-chain or branched C<sub>1</sub>-C<sub>6</sub>-acyl radicals, with the proviso that if R<sup>1</sup> is a straight-chain or branched C<sub>1</sub>-C<sub>6</sub>-acyl radical, R<sup>2</sup> can also be hydrogen, or R<sup>1</sup> and R<sup>2</sup> may combine to form a -(CH<sub>2</sub>)<sub>m</sub>- alkylene radical where m is 4, 5, 6, or 7, wherein one or two CH<sub>2</sub> groups can be replaced by O and/or NH and/or one or two CH<sub>2</sub> groups can be substituted by methyl, and

Z is O, S, or NH,

(III) optionally, further NCO-reactive compounds containing anionic, cationic, and/or potentially anionic or cationic groups, and

(IV) optionally, further auxiliary and additive substances.

18. A nonfelting wool according to Claim 17 wherein the organic polyisocyanate is a unmodified aliphatic, cycloaliphatic, araliphatic, or aromatic isocyanate having an average NCO functionality of 1.8 to 4.2.

19. A nonfelting wool according to Claim 17 wherein the polyalkylene oxide alcohol, amine, and/or thiol contains on average 6 to 60 alkylene oxide units per molecule.

20. A nonfelting wool according to Claim 19 wherein the polyalkylene oxide alcohol, amine, and/or thiol is a polyethylene oxide/propylene oxide alcohol, amine, and/or thiol.

21. A nonfelting wool according to Claim 19 wherein the polyethylene oxide/propylene oxide alcohol, amine, and/or thiol contains not less than 60 mol% of ethylene oxide units, based on the sum total of ethylene oxide and propylene oxide units.

22. A nonfelting wool according to Claim 17 wherein the NCO-reactive compound is

- (i) a hydroxyl- or amino-functional compound having tertiary amino groups,
- (ii) a hydroxyl- or amino-functional compound having carboxyl or sulphonic acid groups,

- (iii) a hydroxyl- or amino-functional compound having carboxylate or sulphonate groups for which the counterions are metal cations of the alkali metal or alkaline earth metal group or ammonium ions, or
- (iv) a hydroxyl- or amino-functional compound having ammonium groups obtained from the tertiary amino groups of the compounds (i) by alkylation or protonation.

23. A nonfelting wool according to Claim 17 wherein the softeners is a fatty acid amide, ester quat, quaternary fatty acid amide, betaine, fatty acid sarcoside, aminosilicone, polyethylene wax emulsion or silicone emulsion.

24. A nonfelting wool according to Claim 17 wherein the antislip agent is an anionic or cationic silica sol, blocked isocyanate resin, hydrophilicized isocyanate resin, polyacrylate, or polyvinyl alcohol.

25. A process for the antifelt finishing of wool comprising exposing wool to

- (a) a plasma in a pretreatment, followed by
- (b) optionally, an aqueous dispersion of self-dispersing isocyanates,
- (c) a softener, and
- (d) optionally, an antislip agent.

26. A process for the antifelt finishing of wool according to Claim 25 wherein exposure to the aqueous dispersion of self-dispersing isocyanates is effected either batchwise in an exhaust process or continuously by dipping, roll application, padding, application of a mist or spray, or backwasher application.

27. A process for the antifelt finishing of wool according to Claim 25 wherein exposure to the aqueous dispersion of self-dispersing isocyanates and the softener is effected are carried out together and are followed by exposure to the antislip agent.--

Figure 1 shows the results of the 1000 iterations of the MCMC algorithm. The trace plots for the parameters  $\alpha$ ,  $\beta$ ,  $\gamma$ ,  $\delta$ ,  $\epsilon$ ,  $\zeta$ ,  $\eta$ ,  $\theta$ ,  $\phi$ , and  $\psi$  are displayed. The trace plots for  $\alpha$ ,  $\beta$ ,  $\gamma$ ,  $\delta$ ,  $\epsilon$ ,  $\zeta$ ,  $\eta$ ,  $\theta$ , and  $\phi$  show good mixing and convergence to a stationary distribution. The trace plot for  $\psi$  shows a very slow convergence, indicating a high degree of autocorrelation. The mean values for the parameters are summarized in Table 1.

--WO 00/37734

- 24 -

### ABSTRACT OF THE DISCLOSURE

- (a) a plasma in a pretreatment, followed by
- (b) optionally, an aqueous dispersion of self-dispersing isocyanates,
- (c) a softener, and
- (d) optionally, an antislip agent.--

REMARKS

Applicants hereby offer preliminary amendments to the present application to place the application in better form for allowance.

Applicants have canceled Claims 1-13 in favor of replacement Claims 14-27 to correct certain informalities (including removal of preferences or addition of new claims for such preferences) and to clarify the intended meaning of the claims. Applicants respectfully submit that the claims are fully supported in the specification.

Applicants have amended the specification to change the title to correspond to the English version of the title appearing on the International Application and to capitalize all letters in the title. Applicants submit that these amendments serve only to clarify their application and do not alter the scope of their disclosure.

Applicants have added an Abstract that summarizes the subject matter of their invention. A copy of the new Abstract is separately attached.

In view of the preceding amendments and remarks, allowance of the claims is respectfully requested.

Respectfully submitted,

By Richard E.L. Henderson  
Richard E.L. Henderson  
Attorney for Applicants  
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s:/sr/reih0330



**ANNOTATED VERSION OF AMENDMENTS**

**IN THE SPECIFICATION:**

The title at page 1, line 1, has been changed from "**Nonfelting wool and antifelt finishing process**" to

--WOOL WITH ANTIFELT FINISH AND  
**METHOD FOR PROVIDING AN ANTIFELT FINISH--**

**IN THE CLAIMS:**

The heading for the claims at page 20 , line 1 has been changed from  
"**Claims**" to --**WHAT IS CLAIMED IS:**--

Claims 1-13 have been canceled in favor of replacement Claims 14-27.

--14. A nonfelting wool obtained by a process comprising exposing wool to

- (a) a plasma in a pretreatment, followed by
- (b) optionally, an aqueous dispersion of self-dispersing isocyanates,
- (c) a softener, and
- (d) optionally, an antislip agent.

15. A nonfelting wool obtained by a process comprising exposing wool to

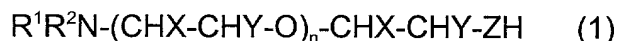
- (a) a plasma in a pretreatment, followed by
- (b) an aqueous dispersion of self-dispersing isocyanates,
- (c) a softener, and
- (d) optionally, an antislip agent.

16. A nonfelting wool according to Claim 14 wherein the wool is raw wool obtained after a raw wool scour, dyed or undyed wool slubbing, or a dyed or undyed wool yarn, knit, or cloth.

17. A nonfelting wool according to Claim 14 wherein the self-dispersing isocyanate has an isocyanate content of 1 to 25% by weight, reckoned as NCO (having a molecular weight of 42 g/mol), and is obtained by reaction in any order of

- (l) organic polyisocyanates having an average NCO functionality of 1.8 to 4.2  
with

- (II) polyalkylene oxide alcohols, amines, and/or thiols of the formula (1)



wherein

n is 3 to 70,

X and Y are hydrogen or methyl, with the proviso that when one of X and Y is methyl the other of X and Y must be hydrogen,

R<sup>1</sup> and R<sup>2</sup> are independently straight-chain or branched C<sub>1</sub>-C<sub>6</sub>-alkyl radicals or straight-chain or branched C<sub>1</sub>-C<sub>6</sub>-acyl radicals, with the proviso that if R<sup>1</sup> is a straight-chain or branched C<sub>1</sub>-C<sub>6</sub>-acyl radical, R<sup>2</sup> can also be hydrogen, or R<sup>1</sup> and R<sup>2</sup> may combine to form a -(CH<sub>2</sub>)<sub>m</sub>-alkylene radical where m is 4, 5, 6, or 7, wherein one or two CH<sub>2</sub> groups can be replaced by O and/or NH and/or one or two CH<sub>2</sub> groups can be substituted by methyl, and

Z is O, S, or NH,

- (III) optionally, further NCO-reactive compounds containing anionic, cationic, and/or potentially anionic or cationic groups, and  
(IV) optionally, further auxiliary and additive substances.

18. A nonfelting wool according to Claim 17 wherein the organic polyisocyanate is a unmodified aliphatic, cycloaliphatic, araliphatic, or aromatic isocyanate having an average NCO functionality of 1.8 to 4.2.

19. A nonfelting wool according to Claim 17 wherein the polyalkylene oxide alcohol, amine, and/or thiol contains on average 6 to 60 alkylene oxide units per molecule.

20. A nonfelting wool according to Claim 19 wherein the polyalkylene oxide alcohol, amine, and/or thiol is a polyethylene oxide/propylene oxide alcohol, amine, and/or thiol.

21. A nonfelting wool according to Claim 19 wherein the polyethylene oxide/propylene oxide alcohol, amine, and/or thiol contains not less than 60 mol% of ethylene oxide units, based on the sum total of ethylene oxide and propylene oxide units.

22. A nonfelting wool according to Claim 17 wherein the NCO-reactive compound is

- (i) a hydroxyl- or amino-functional compound having tertiary amino groups,
- (ii) a hydroxyl- or amino-functional compound having carboxyl or sulphonic acid groups,
- (iii) a hydroxyl- or amino-functional compound having carboxylate or sulphonate groups for which the counterions are metal cations of the alkali metal or alkaline earth metal group or ammonium ions, or
- (iv) a hydroxyl- or amino-functional compound having ammonium groups obtained from the tertiary amino groups of the compounds (i) by alkylation or protonation.

23. A nonfelting wool according to Claim 17 wherein the softeners is a fatty acid amide, ester quat, quaternary fatty acid amide, betaine, fatty acid sarcoside, aminosilicone, polyethylene wax emulsion or silicone emulsion.

24. A nonfelting wool according to Claim 17 wherein the antislip agent is an anionic or cationic silica sol, blocked isocyanate resin, hydrophilicized isocyanate resin, polyacrylate, or polyvinyl alcohol.

25. A process for the antifelt finishing of wool comprising exposing wool to

- (a) a plasma in a pretreatment, followed by
- (b) optionally, an aqueous dispersion of self-dispersing isocyanates,
- (c) a softener, and
- (d) optionally, an antislip agent.

26. A process for the antifelt finishing of wool according to Claim 25 wherein exposure to the aqueous dispersion of self-dispersing isocyanates is effected either batchwise in an exhaust process or continuously by dipping, roll application, padding, application of a mist or spray, or backwasher application.

27. A process for the antifelt finishing of wool according to Claim 25 wherein exposure to the aqueous dispersion of self-dispersing isocyanates and the softener is effected are carried out together and are followed by exposure to the antislip agent.--

**IN THE ABSTRACT:**

An Abstract has been added as new page 24 as follows:

--WO 00/37734

PCT/EP99/09527

- 24 -

**WOOL WITH ANTIFELT FINISH AND  
METHOD FOR PROVIDING AN ANTIFELT FINISH**

**ABSTRACT OF THE DISCLOSURE**

The invention relates to nonfelting wool obtained by exposing wool to

- (a) a plasma in a pretreatment, followed by
- (b) optionally, an aqueous dispersion of self-dispersing isocyanates,
- (c) a softener, and
- (d) optionally, an antislip agent.--

09/868211 0 1 4 JUN 2001

**PCT**WELTORGANISATION FÜR GEISTIGES EIGENTUM  
Internationales BüroINTERNATIONALE ANMELDUNG VERÖFFENTLICHT NACH DEM VERTRAG ÜBER DIE  
INTERNATIONALE ZUSAMMENARBEIT AUF DEM GEBIET DES PATENTWESENS (PCT)(51) Internationale Patentklassifikation <sup>7</sup> :  
D06M 10/02, 15/568, 15/21 // 101:12

A1

(11) Internationale Veröffentlichungsnummer: WO 00/37734

(43) Internationales  
Veröffentlichungsdatum: 29. Juni 2000 (29.06.00)

(21) Internationales Aktenzeichen: PCT/EP99/09527

(22) Internationales Anmeldedatum: 6. Dezember 1999 (06.12.99)

(30) Prioritätsdaten:  
198 58 734.1 18. Dezember 1998 (18.12.98) DE(71) Anmelder (für alle Bestimmungsstaaten ausser US): BAYER  
AKTIENGESELLSCHAFT [DE/DE]; D-51368 Leverkusen  
(DE).

(72) Erfinder; und

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KÜMMELER, Ferdinand [DE/DE]; Rheindorfer Strasse  
63a, D-51371 Leverkusen (DE).(74) Gemeinsamer Vertreter: BAYER AKTIENGE-  
SELLSCHAFT; D-51368 Leverkusen (DE).(81) Bestimmungsstaaten: AE, AL, AM, AT, AU, AZ, BA, BB,  
BG, BR, BY, CA, CH, CN, CR, CU, CZ, DE, DK, DM, EE,  
ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP,  
KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA,  
MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU,  
SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, TZ, UA, UG,  
US, UZ, VN, YU, ZA, ZW, ARIPO Patent (GH, GM, KE,  
LS, MW, SD, SL, SZ, TZ, UG, ZW), eurasisches Patent  
(AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), europäisches  
Patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR,  
IE, IT, LU, MC, NL, PT, SE), OAPI Patent (BF, BJ, CF,  
CG, CI, CM, GA, GN, GW, ML, MR, NE, SN, TD, TG).

Veröffentlicht

Mit internationalem Recherchenbericht.

(54) Title: WOOL WITH ANTIFELT FINISH AND METHOD FOR PROVIDING AN ANTIFELT FINISH

(54) Bezeichnung: FILZFREI AUSGERÜSTETE WOLLE UND VERFAHREN ZUR FILZFREIAUSRÜSTUNG

(57) Abstract

The invention relates to wool having an antifelt finish which in a first step a) is subjected to a plasma, in step b) is possibly treated with an aqueous dispersion of self-dispersing isocyanates, in step c) is treated with a softener and in step d) is possibly treated with an agent conferring an antislip finish. The wool treated in this manner is characterized by not only an excellent antifelt finish but also very good handling properties.

(57) Zusammenfassung

Es wird filzfrei ausgerüstete Wolle bereitgestellt, die in einem ersten Schritt a) einem Plasma ausgesetzt wird, dann gegebenenfalls in Schritt b) mit einer wässrigen Dispersion selbstdispersierender Isocyanate behandelt wird, anschließend in Schritt c) mit einem Weichmacher sowie in Schritt d) abschließend gegebenenfalls mit einem Schiebefestmittel behandelt wird. Die so behandelte Wolle besitzt nicht nur eine exzellente Filzfreiausrüstung, sondern auch sehr gute Griff Eigenschaften.

09/868211

PCT/PTO 1 4 JUN 2001

Nonfelting wool and antifelt finishing process

The invention relates to nonfelting wool and to a process for antifelt finishing by treating the wool with a plasma, followed by an aftertreatment with various finishes.

5

The textile processing industry has a particular interest in reducing the felting tendency of wool, especially of raw wool or unprocessed wool. The felting of wool is customarily reduced by finishing with specific auxiliaries.

- 10 Isocyanates for the antifelt finishing of textiles are well known and can be used, for example as described in DE-A-19 04 802, in organic solvents or, as described in DE-A-17 69 121, in aqueous dispersion with the aid of emulsifiers. Both organic solvents and possibly water-polluting emulsifiers are today no longer appropriate for ecological and occupational hygiene reasons. Prior artisans therefore developed self-
- 15 dispersing isocyanates and also formulations containing very low levels of solvents or emulsifiers as auxiliaries and additives.

- DE-A-1 794 221 describes the treatment of fibre materials with isocyanate prepolymers which still contain free isocyanate groups; this finishing process can
- 20 take place in solvents such as perchloroethylene or in aqueous emulsion by using auxiliary emulsifiers.

US-A-3,847,543 discloses a process for the antifelt finishing of wool using an aqueous dispersion containing at one and the same time aliphatic isocyanates, OH-functional crosslinkers and organometallic catalysts. Although this process takes place in an aqueous phase, auxiliary solvents and emulsifiers continue to be required.

DE-A-26 57 513 describes a process for the antifelt finishing of wool by treating the wool yarn with an aqueous liquor which contains the feltproofing agent. The feltproofing agents used are reactive polyolefins, reaction products of polyisocyanates and hydroxyl compounds, silicone polymers, aziridine compounds, reaction products of epoxides with fatty amines and dicarboxylic acids or polyamides, reaction products with thiosulphate end groups or preferably reaction products with mercapto end groups.

WO 95/30045 describes a process utilizing specific isocyanates for the antifelt finishing of wool. No solvents or emulsifiers are needed because the isocyanates used

"Express Mail" mailing label number LT146886964US  
Date of Deposit June 14, 2001

I hereby certify that this paper or fee is being deposited with the United States Postal Service "Express Mail Post Office to Addressee" service under 37 CFR 1.10 on the date indicated above and is addressed to the Assistant Commissioner of Patents and Trademarks, Washington, D.C. 20231

Dorothy P. Colangelo

(Name of person mailing paper or fee)

Signature of person mailing paper or fee

LA 33233

are water-dispersible. The wool is first subjected to a pretreatment with oxidizing agents, followed by a reductive treatment, before the water-dispersible isocyanates are used.

- 5 The prior art further includes another method for the antifelt finishing of wool where the wool is treated with a plasma. DE-A-43 44 428 discloses for example a process where the wool is subjected to an antifelt finish comprising a combination of plasma or corona pretreatment and enzymatic aftertreatment. The wool is sensitized with a solution which contains sulphide ions prior to the enzyme treatment.

10

DE 196 16 776 C1 further describes a process for the antifelt finishing of wool where moist wool material having a water content of 4-40% by weight is subjected to a low pressure plasma treatment before being further processed into textile fabrics or sheets. The wool is exposed to a radio frequency discharge of a frequency of  
15 1 kHz-3 GHz and a power density of  $0.001-3 \text{ W/cm}^3$  at a pressure of  $10^{-2}$ -10 mbar for a period of 1-600 sec in the presence or absence of non-polymerizing gases.

20

The German Patent Application bearing the file reference 197 36 542.6, unpublished at the priority date of the present invention, discloses a process for the antifelt finishing of wool where the wool is initially likewise exposed to a low pressure plasma and subsequently aftertreated with aqueous dispersions of self-dispersing isocyanates.

25

All the aforementioned processes for the antifelt finishing of wool have the shared disadvantage that applying the antifelt finishes has an adverse effect on the hand properties of the wool. The treated wool materials are frequently observed to have a strawy hand.

30

The present invention accordingly has for its object to provide wool which is nonfelting, i.e. felts or shrinks only insignificantly, if at all, in machine washing after further processing into made-up merchandise, and has improved hand properties.

35

The present invention provides nonfelting wool, characterized in that the wool is

- a) exposed to a plasma in a pretreatment,
- b) optionally with an aqueous dispersion of self-dispersing isocyanates,
- c) then with a softener and
- d) finally optionally with an antislip agent.

Preferably the nonfelting wool is

- a) exposed to a plasma in a pretreatment,
- b) with an aqueous dispersion of self-dispersing isocyanates,
- 5 c) then with a softener and
- d) optionally finally with an antislip agent.

The present invention further provides the process for the antifelt finishing of wool, characterized in that the wool is

- 10 a) exposed to a plasma in a pretreatment,
  - b) optionally with an aqueous dispersion of self-dispersing isocyanates,
  - c) then with a softener and
  - d) finally optionally with an antislip agent.
- 15 Preference here is likewise given to a process for the antifelt finishing of wool that is characterized in that the wool is
- a) exposed to a plasma in a pretreatment,
  - b) with an aqueous dispersion of self-dispersing isocyanates,
  - c) then with a softener and
  - 20 d) optionally finally with an antislip agent.

The plasma treatment of the wool as per step a) in the process of the invention can be effected either in the form of a low temperature plasma treatment at reduced pressure or in the form of a corona treatment.

25

- The wool used may be selected from a very wide range of wool materials, for example raw wool after the raw wool scour, dyed or undyed wool slubbing, dyed or undyed wool yarn, knits or cloths. The water content of the wool is customarily 4 40% by weight, preferably 5 to 30% by weight, particularly preferably 6 25% by weight, especially 8 15% by weight.
- 30

- The low temperature plasma treatment is described at length in DE 196 16 776 C1, incorporated herein by reference. The wool is subjected to a high frequency discharge having a frequency of 1 kHz - 3 GHz and a power density of 0.001 - 35 3 W/cm<sup>3</sup> at a pressure of 10<sup>-2</sup> - 10 mbar for a period of 1 - 600 seconds in the presence or absence of non-polymerizing gases.



The treatment is preferably effected under a pressure of 0.1 - 1 mbar and for a period of 2 - 5 minutes.

The actual low temperature plasma is generated by feeding in electromagnetic radiation in the frequency range of 1 kHz - 3 GHz. In a preferred variant, the low temperature plasma is generated via a microwave discharge of 1 - 3 GHz (the power density at the outcoupling is especially 0.1 - 15 W/cm<sup>2</sup>). The electromagnetic radiation can be supplied continuously or pulsed. A pulsed high frequency discharge having a pulsing frequency of up to 10 kHz is especially advantageous.

When non-polymerizing gases are additionally used as plasma process gases, they are introduced into the plasma treatment space at a flow rate of up to 200 l/h. Useful non-polymerizing gases are in particular oxygen, nitrogen, noble gases, especially argon, air or mixtures thereof.

The design and construction of a low temperature plasma reactor are known per se. Preference is given to using an electrodeless reactor having an outcoupling for microwaves. The wool to be treated is preferably placed underneath the outcoupling unit. The distance of the wool from the outcoupling unit is preferably 1 - 30 cm, especially 2 - 10 cm. After the wool to be treated has been introduced into the reactor, the reactor is suitably evacuated with vacuum pumps in such a way that the pressure during the plasma treatment is in the range of 10<sup>-2</sup> - 10 mbar, preferably 0.1 - 1 mbar. A continuous flow-through operation is preferably carried out by applying specific vacuum locks which make it possible for the material to enter and exit without leakage.

Alternatively to this embodiment of the low temperature plasma treatment under low pressure, the wool can also be subjected to a corona treatment at a pressure in the range of 100 mbar - 1.5 bar, preferably at atmospheric pressure. The corona treatment is described in detail in a coterminously filed German patent application.

The corona treatment subjects the wool to a high frequency discharge having a power density of customarily 0.01-5 Ws/cm<sup>2</sup> for a period of 1-60 seconds, preferably 2-40 seconds, particularly 3-30 seconds, in the presence or absence of non-polymerizing gases. Suitable non-polymerizing gases are air, oxygen, nitrogen, noble gases or mixtures thereof.

The actual plasma is generated by applying an alternating voltage of 1-20 kV in the frequency range between 1 kHz-1 GHz, preferably 1-100 kHz, to electrodes, one or both poles being provided with an insulator material. The alternating voltage can be supplied either continuously or with individual pulses or with pulse trains and pauses in between.

The design and apparatus configurations of a corona reactor are known per se and described for example in the German Application bearing the file reference 197 31 562, unpublished at the priority date of the present invention. The corona treatment is preferably carried out via electric discharges in the atmospheric pressure region, for which the wool to be treated is initially introduced into a sealed, tight treatment housing, charged there with the working gas, i.e. the abovementioned non-polymerizing gas, and subsequently exposed to an electric barrier discharge in a gap between the two treatment electrodes. The distance of the wool material from the treatment electrodes is 0-15 mm, preferably 0.1-5 mm, particularly 0.3-2 mm. The treatment electrodes are preferably constructed as rotatable rolls either or both of which are coated with electrically refractory dielectric material.

Performing the corona treatment at a pressure in the range from 100 mbar to 1.5 bar, preferably at atmospheric pressure, has the advantage over the low pressure plasma treatment at  $10^{-2}$  - 10 mbar that the equipment needed is very much less complicated than in the case of the low pressure treatment. Vacuum pumps are not required, nor is it necessary to fit special vacuum locks.

The special effect of the plasma treatment in step a) of the process of the invention might be explained as follows. The liquid present in the fibre desorbs from the fibre surface as water vapour/gas during the process. High energy electrons, ions and also highly excited neutral molecules or radicals are formed and act on the surface of the fibre, the water vapour desorbed from the fibre ensuring that particularly reactive particles are formed in the immediate vicinity of the respective fibre surface and these particularly reactive particles act on the surface.

Following the plasma treatment of wool in step a) an aftertreatment is carried out with various finishes. The facultative step b) comprises the treatment of the wool with an aqueous dispersion of self-dispersing isocyanates. Preferably step b) is carried out in the process of the invention. Useful self-dispersing isocyanates form part of the subject-matter of the German Patent Application bearing the reference

number 197 36 542.6, unpublished at the priority date of the present invention. They have an isocyanate content of 1-25% by weight, reckoned as NCO (having a molecular weight of 42 g/mol), and are obtainable by reaction in any order of

5 I) organic polyisocyanates having an average NCO functionality of 1.8 - 4.2 with

II) polyalkylene oxide alcohols, amines and/or thiols of the formula 1



where

n is 3-70,

15 X and Y are hydrogen or methyl with the proviso that when one of X and Y is methyl the other must be hydrogen,

20  $R^1$  and  $R^2$  are independently straight-chain or branched  $C_1$ - $C_6$ -alkyl radicals or straight-chain or branched  $C_1$ - $C_6$ -acyl radicals, with the proviso that if  $R^1$  is a straight-chain or branched  $C_1$ - $C_6$ -acyl radical,  $R^2$  can also be hydrogen, and, furthermore,  $R^1$  and  $R^2$  may also combine to form a  $-(CH_2)_m$ - alkylene radical where  $m = 4, 5, 6$  or  $7$ , wherein one or two  $CH_2$  groups can be replaced by O and/or NH and/or one or two  $CH_2$  groups can be substituted by methyl, and

25 Z is O, S or NH,

30 and optionally

III) further NCO-reactive compounds containing anionic, cationic and/or potentially anionic or cationic groups,

35 and optionally

IV) further auxiliary and additive substances.

For the purposes of the present invention, "self-dispersing" means that the isocyanates produce fine dispersions having particle sizes of <500 nm (measured by ultracentrifuge) in water when in a concentration of up to 70% by weight, preferably up to 50% by weight.

Examples of useful starting materials for the self-dispersing isocyanates are:

- I) Unmodified (i.e. not previously reacted with OH-functional compounds), aliphatic, cycloaliphatic, araliphatic or aromatic polyisocyanates having an average NCO functionality of 1.8 to 4.2. Preference is given to using aliphatic, cycloaliphatic, araliphatic or aromatic polyisocyanates which have uretdione and/or isocyanurate and/or allophanate and/or biuret and/or oxadiazine structures and which are preparable from aliphatic, cycloaliphatic, araliphatic or aromatic diisocyanates in a conventional manner.

Suitable examples of aliphatic and cycloaliphatic diisocyanates are 1,4-diisocyanatobutane, 1,6-diisocyanatohexane, 1,5-diisocyanato-2,2-dimethylpentane, 2,2,4- and 2,4,4-trimethyl-1,6-diisocyanatohexane, 1,3- and 1,4-diisocyanatocyclohexane, 1-isocyanato-3,3,5-trimethyl-5-isocyanatomethylcyclohexane, 1-isocyanato-1-methyl-4-isocyanatomethylcyclohexane and 4,4-diisocyanatodicyclohexylmethane or any mixtures of such diisocyanates.

Examples of suitable aromatic diisocyanates are tolylene diisocyanate, 1,5-diisocyanatonaphthalene and diphenylmethane diisocyanate.

The preferred polyisocyanates, which contain uretdione and/or isocyanurate and/or allophanate and/or biuret and/or oxadiazine groups and having an NCO content of 19 to 24% by weight which consist essentially of trimeric reaction products of 1,6-diisocyanatohexane or 1-isocyanato-3,3,5-trimethyl-5-isocyanatomethylcyclohexane and of the corresponding higher homologues.

Particular preference is given to using the corresponding polyisocyanates of the mentioned average NCO content which are substantially free of uretdione groups and have isocyanate groups and which are obtainable by conventional, catalytic trimerization of 1,6-diisocyanatohexane or 1-isocyanato-3,3,5-tri-

5 methyl-5-isocyanatomethyl-cyclohexane with isocyanurate formation and which preferably have an average NCO functionality of 3.2 to 4.2. Preference is also given to the trimeric polyisocyanates having an average NCO content of 19 to 24% by weight which are obtained in a conventional manner by reaction of 1,6-diisocyanatohexane with a deficiency of water or in the presence of water-eliminating reactants and which have essentially biuret groups.

10 II) Of the polyalkylene oxide alcohols, amines and/or thiols of the formula 1, the polyalkylene oxide alcohols are preferred ( $Z = O$  in formula 1). The polyalkylene oxide alcohols can be reacted with  $NH_3$  to form polyalkylene oxide amines ( $Z = NH$  in formula 1) and with  $H_2S$  to form polyalkylene oxide thiols ( $Z = S$  in formula 1).

15 The polyalkylene oxide alcohols thus underlying the polyalkylene oxide amines and thiols too contain on average 3-70, preferably 6-60, especially 7-20, alkylene oxide units per molecule and are obtainable in a conventional manner by alkoxylation of suitable starter molecules. The starter molecules used can be compounds of the formula  $R^1R^2NH$ . Depending on the meanings of  $R^1$  and  $R^2$ , they are secondary amines or amides. According to the definition of  $R^1$  and  $R^2$  mentioned for the formula 1, the alkoxylation reaction can also be started using morpholine as heterocyclic nitrogen compound. Identical compounds are further obtained on using compounds of the formula  $R^1R^2N-CHX-CH-OH$ , for example 2-morpholinoethanol, as starter molecules  
20 for the alkoxylation reaction. Further useful starters include for example acylation products of ethanolamine, for example acetyethanolamine.

30 Alkylene oxides suitable for the alkoxylation reaction are in particular ethylene oxide and propylene oxide, which can be used in the alkoxylation reaction individually or in any desired order or else mixed. The polyalkylene oxide alcohols are in this case based either on pure polyethylene oxides or on mixed polyethylene oxides/propylene oxides. In particularly suitable polyalkylene oxide alcohols, there are on average 3-70, preferably 6-60 and in particular 7-20, alkylene oxide units per molecule and not less than 60 mol%, preferably not less than 70 mol%, of the alkylene oxide units are ethylene  
35 oxide units.

III) The NCO-reactive compounds which contain anionic, cationic and/or potentially anionic or cationic groups are customarily

5 i) hydroxyl- or amino-functional compounds having tertiary amino groups as described in the German Patent Application DE-A-43 19 571, which is hereby expressly incorporated herein,

10 ii) hydroxyl- or amino-functional compounds having carboxyl or sulphonic acid groups as described in the German Patent Application DE-A-195 20 092, which is hereby expressly incorporated herein,

15 iii) hydroxyl- or amino-functional compounds having carboxylate or sulphonate groups whose counterions are metal cations of the alkali metal or alkaline earth metal group or ammonium ions, as likewise described in DE-A-195 20 092,

20 iv) hydroxyl- or amino-functional compounds having ammonium groups which are obtainable in a conventional manner from the tertiary amino groups of the compounds i) by alkylation or protonation as described in EP-A 0 582 166.

25 The process of the invention, as will be appreciated, may also be carried out using any desired mixtures of such NCO-reactive compounds, if chemically sensible, for example of the groups i) and iv) or of the groups ii) and iv).

30 IV) The optional auxiliary and additive substances are for example wetting agents, surfactants, foam inhibitors or absorption assistants. These auxiliary and additive substances can either be inert or else reactive towards the isocyanate groups.

35 The unmodified polyisocyanates I to be used according to the invention can also be used in combination with external i.e. additional ionic or nonionic emulsifiers. Such emulsifiers are described for example in Methoden der organischen Chemie, Houben-Weyl, vol. XIV/1, part 1, page 190-208 Thieme-Verlag, Stuttgart (1961), in US Patent 3,428,532 and EP-A 0,013,112. The emulsifiers are used in an amount sufficient to ensure dispersibility.

If initially polyisocyanates I) are reacted with polyalkylene oxide alcohols II), this reaction can be carried out in a conventional manner, by maintaining an NCO/OH equivalents ratio of at least 2:1, generally of 4:1 to about 1000:1. Polyethylene oxide alcohols are used. To obtain polyethylene oxide-modified polyisocyanates having an average NCO functionality of from 1.8 to 4.2, preferably of 2.0 to 4.0, containing 12.0 to 21.5% by weight of aliphatically or cycloaliphatically attached isocyanate groups and containing 2 to 20% by weight of ethylene oxide units (reckoned as C<sub>2</sub>H<sub>4</sub>O, molecular weight = 44 g/mol) within the polyethylene oxide chains, the polyethylene oxide chains having on average 3 to 70 ethylene oxide units.

The starting components I), II) and optionally III) can be reacted in any desired order in the absence of moisture, preferably without solvent. An increasing amount of component (II) will lead to a higher end-product viscosity. If the viscosity rises above 100 mPas, it is advantageous to carry out the process in the presence of a solvent which is preferably miscible with water but inert towards the polyisocyanate. Suitable solvents are, for example, alkyl ether acetates, glycol diesters, toluene, carboxylic esters, acetone, methyl ethyl ketone, tetrahydrofuran and dimethylformamide.

Conventional catalysts such as dibutyltin dilaurate, tin(II) octoate or 1,4-diazabicyclo[2,2,2]octane in amounts of 10 to 1000 ppm, based on the components I), II) and optionally III), can be used to speed up the reaction of the components. The reaction is carried out in the temperature range up to 130°C, preferably in the range between 10°C and 100°C, particularly preferably between 20°C and 80°C. The reaction is monitored by determining the NCO content by titration or by measurement of the IR spectra and evaluation of the NCO band at 2260-2275 cm<sup>-1</sup> and is terminated when the isocyanate content is not more than 0.1% by weight above the value which is obtained at complete conversion under the given stoichiometry. In general, reaction times of less than 24 hours are sufficient. Preference is given to the solvent-free synthesis of the self-dispersing isocyanates to be used according to the invention.

In a further embodiment, it is also possible to prepare the self-dispersing isocyanates to be used according to the invention in step b) by mixing

- 1) unmodified polyisocyanates I)

2) polyisocyanates obtained by reaction of polyisocyanates I) with the NCO-reactive compounds III) at an equivalents ratio of the NCO-reactive groups of compounds III) to the NCO groups of component II, which are used, of 1:1 to 1:1000, and

3) polyisocyanates obtained by reaction of polyisocyanates I) with polyalkylene oxide alcohols, amines and/or thiols II), at an equivalents ratio of the NCO-reactive groups of component II to the NCO groups of component I), which are used, of 1:1 to 1:1000.

In this preparation variant, the person skilled in the art must make use of appropriate initial weights to control the number of the NCO-reactive equivalents, the polyalkylene oxide content, the NCO content and the NCO functionality in such a way that the mixture obtained has the composition required for water dispersibility, subject in particular to the preferred ranges already mentioned.

The self-dispersible isocyanates are industrially readily handleable and stable for many months in storage in the absence of moisture.

The self-dispersible isocyanates are preferably used without organic solvents in step b) of the process according to the invention. Due to their self-dispersibility, they are very easy to emulsify in water at temperatures up to 100°C without being subjected to high shearing forces. The isocyanate concentration of the emulsion can be up to 70% by weight. However, it is more advantageous to prepare emulsions having an isocyanate concentration of up to 50% by weight. Emulsification may be accomplished using the mixing assemblies customary in the art (stirrers, mixers of the rotor-stator type and, for example, high pressure emulsifying machines). In general, a static mixer is sufficient. The emulsions obtained have a processing time of up to 24 hours, which depends on the structure of the self-dispersible isocyanates used, in particular on their content of basic nitrogen atoms.

The treatment of the wool with the aqueous dispersion of the self-dispersing isocyanates in step b) is effected according to customary processes of the prior art. Suitable is for example a batchwise method by the exhaust process or a continuous method by dipping, roll application, padding, application of a mist or spray or backwasher application optionally using dyeing machines, stirrers, etc. to agitate the



treatment liquor. The liquor ratio is choosable within wide limits and can be within the range of (20-5):1, preferably (10-5):1.

5 Step c) of the process according to the invention utilizes the following classes of substances as softeners: fatty acid amides, ester quats, quaternary fatty acid amides, betaines, fatty acid sarcosides, aminosilicones, polyethylene wax emulsions, silicone emulsions.

10 Step d) of the process according to the invention optionally treats the wool material with antislip agents. Antislip agents are finishes to prevent the mutual displacement of weft and warp threads in wovens and loop-formed knits produced later from the wool. There are antislip agents that will cause roughening of the fibre surface and antislip agents capable of dulling the fibre surface and of adhering the threads.

15 Useful antislip agents for roughening the fibre surface include in particular silica sols. These are aqueous solutions of approximately spherical, colloiddally undissolved polysilicic acid molecules having an  $\text{SiO}_2$  content of customarily 30 - 60%. Such silica sols are storable for years without undergoing any changes. Depending on the size of the particles, silica sol is milkily cloudy to colourlessly clear. The average  
20 particle diameter is generally 5 to 150 nm. They are prepared in principle by treating aqueous alkali metal silicate solutions (waterglass) with ion exchangers and stabilizing with little alkali. Silica sols are commercially available in various surface modifications (anionic, cationic or nonionic).

25 Antislip agents that dull the fibre surface and adhere the threads are predominantly synthetic polymer dispersions and natural resins. Useful examples include synthetic polymer dispersions based on polyvinyl, polyacrylic, polymethacrylic, polystyrene or polybutadiene. Particular suitability is possessed by polyvinyl alcohols, polyacrylates and also blocked isocyanate resins and hydrophilicized isocyanate resins.

30 The application of the softeners in step c) and of the antislip agents in step d) of the process according to the invention is effected either batchwise in an exhaust process or continuously by dipping, roll application, padding, application of a mist or spray or backwasher application.

35 The isocyanate b) is used at 0.1-5% by weight, preferably at 0.5 - 2.5% by weight, based on the total weight of the liquor. The softener c) is used at 1 to 4% by weight,

preferably at 2-4% by weight, based on the total weight of the liquor. The antislip agent is used in an amount of 0.1 to 2% by weight, preferably 0.2 to 0.5% by weight, based on the total weight of the liquor.

- 5 In a further embodiment of the process according to the invention, the wool is
- a) after the plasma pretreatment
  - b) treated with the aqueous dispersion of self-dispersing isocyanates and
  - c) finally with a softener.
- 10 The process of the invention thus includes in this case only the two aftertreatment steps b) and c) following step a). In a further variation of this embodiment, step a) can also be initially followed by the aftertreatment with the softener c) and subsequently with the treatment with the aqueous dispersion of self-dispersing isocyanates b). Another possibility is a conjoint treatment of the plasma treated wool
- 15 with the softener c) and the aqueous dispersion of self-dispersing isocyanates b).

- In a further preferred embodiment, the process according to the invention includes all three aftertreatment steps b), c) and d) after the plasma pretreatment a). The order of the aftertreatments b), c) and d) of the wool material pretreated as per step a) can also
- 20 be varied to the effect that the treatments b) and c) are carried out together and subsequently the aftertreatment with the antislip agent as per d) is executed. It is also possible to carry out the aftertreatment initially as per c), then as per b) and finally as per d). When an anionic or cationic silica sol is used as antislip agent d), the aftertreatment steps are preferably carried out in the order b), c), d) or c), b), d).

### Examples

Percentages hereinbelow are by weight.

#### 5 B) Self-dispersing isocyanates

##### B1) Self-dispersing isocyanate

85 parts by weight of an isocyanate having an NCO content of 22.5% and consisting essentially of trimeric hexamethylene diisocyanate are reacted at 60°C with 15 parts by weight of an ethylene oxide polyether started on morpholine and having an average molecular weight of 420. The resultant product has an NCO content of 16.5% and a viscosity of 2550 mPas at 25°C. The product is very efficiently dispersible in a water-filled glass beaker simply by stirring with a glass rod. The arithmetic NCO functionality is  $F = 2.76$ .

15

##### B2) Self-dispersing isocyanate

85 parts by weight of an isocyanate having an NCO content of 22.5% and consisting essentially of trimeric hexamethylene diisocyanate are reacted at 60°C with 15 parts by weight of a polyethylene glycol monomethyl ether having an average molecular weight of 350. The resultant product has an NCO content of 17% and a viscosity of 1500 mPas at 25°C. The product is very efficiently dispersible in a water-filled glass beaker simply by stirring with a glass rod. The arithmetic NCO functionality is  $F = 2.7$ .

20

#### 25 C) Softeners

##### C1) Softener

The softener C1 has the following composition:

- 10.3 parts by weight of polydimethylsiloxane
- 30 9.5 parts by weight of amide of myristic acid and ethylenediamine
- 4.0 parts by weight of a C<sub>9</sub>-C<sub>18</sub>-alcohol reacted with 3.6 mol of ethylene oxide
- 0.2 part by weight of isobutanol
- 76.0 parts by weight of water

##### 35 C2) Softener

The softener C2 has the following composition:

- 2.3 parts by weight of amide of stearic acid and technical grade behenic acid with aminoethylethanolamine and N,N-dimethylamino-n-propylamine, quaternized with dimethyl sulphate
- 3.2 parts by weight of polydimethylsiloxane
- 5 17.0 parts by weight of amide of technical grade behenic acid and triethylene-tetramine acidified with acetic acid
- 12.0 parts by weight of cationically emulsified polyethylene oxide wax
- 20.9 parts by weight of fatty acid amide with nonionic emulsifer
- 44.6 parts by weight of water

10

### C3) Softener

The softener C3 has the following composition:

- 80.0 parts by weight of nonionic polyethylene oxidate wax emulsion
- 5.0 parts by weight of polyether siloxane
- 15 1.4 parts by weight of a salt of dibutyl phosphate and diethanolamine
- 1.0 part by weight of a C<sub>12-13</sub>-fatty alcohol reacted with 10 mol of ethylene oxide
- 12.0 parts by weight of water
- 0.6 part by weight of scent

### 20 D) Antislip agents

#### D1) Antislip agent

The antislip agent D1 is a reaction product of:

- 85 parts by weight of a technical grade isocyanate from the trimerization reaction
- 25 of hexamethylene diisocyanate with
- 15 parts by weight of a technical grade polyethylene glycol monomethyl ether having a molecular weight of 350.

#### D2) Antislip agent

30 The antislip agent D2 is a mixture of

- 30 parts by weight of a silica sol cationized with basic aluminium chloride and stabilized with acetic acid and
- 70 parts by weight of water.

### 35 Examples 1-4

(Order of treatment steps: a), c), b))

- First, moist wool slubbing is subjected to a corona treatment (treatment conditions: frequency: 23 kHz; power: 3.7 kW; electrode distance: 0.8 mm; forward feed rate: 10 m/min) and thereafter in a waterbath initially to a treatment with a 2% the aqueous solution of the particular softener. The wet slubbing is then whizzed to spin off excess softener solution. After air drying, the thusly pretreated wool slubbing is treated on a lab pad-mangle with an aqueous dispersion of the particular isocyanate (concentration of the isocyanate: 25 g/l of buffer solution (sodium acetate/glacial acetic acid buffer) to a wet pick-up of 80%. After rinsing out with water and air drying, the slubbing is tested by the Aachen felting ball test (IWTO standard 20-69) for the quality of the antifelt finish. The larger the felting ball diameter and the smaller the felt density, the better the antifelt finish. In addition, 4 people compare the hand of these wool slubbing samples independently to determine the hand ranking (ratings from 1 (best hand) to 12 (worst hand)).
- Table (I) below contains the observed values for the felting ball diameter, the felt density and the hand ranking.

Table (I):

Example	1	2	3	4
Self-dispersing isocyanate	B2	B1	B2	B1
Softener	C1	C1	C2	C2
Felting ball diameter [cm]	2.282	2.246	3.019	2.869
Felt density [g/cm <sup>3</sup> ]	0.161	0.169	0.069	0.081
Hand ranking	12	9	10	7

20

### Examples 5-8

(Order of treatment steps: a), b), c))

- First, moist wool slubbing is subjected to a plasma treatment similarly to Examples 1-4 and then treated on a lab pad-mangle with an aqueous dispersion of the particular self-dispersing isocyanate (concentration of the isocyanate: 25 g/l of buffer solution (sodium acetate/glacial acetic acid buffer) to a wet pick-up of 80%. After air drying, the thusly pretreated wool slubbing is treated in a waterbath with a 2% aqueous solution of the particular softener. The wet slubbing is then whizzed to spin off excess softener solution. After rinsing out with water and air drying, the slubbing is

30

tested by the Aachen felting ball test (IWTO standard 20-69) for the quality of the antifelt finish. In addition, 4 people compare the hand of these wool slubbing samples independently to determine the hand ranking.

- 5 Table (II) below contains the observed values for the felting ball diameter, the felt density and the hand ranking.

Table (II):

Example	5	6	7	8
Self-dispersing isocyanate	B2	B1	B2	B1
Softener	C1	C1	C2	C2
Felting ball diameter [cm]	2.842	3.189	3.181	2.681
Felt density [g/cm <sup>3</sup> ]	0.083	0.059	0.059	0.099
Hand ranking	2	4	6	1

10

**Examples 9-12:**

(Order of treatment steps: a), b), c), d))

- 15 First, moist wool slubbing is subjected to a plasma treatment as described in Examples 1-4 and then treated on a lab pad-mangle with an aqueous dispersion of the particular self-dispersing isocyanate (concentration of the isocyanate: 25g/e of sulfur solution (sodium acetate/glacial acetic acid sulfur)) to a wet pick-up of 80%. After rinsing out with water and air drying the thusly pretreated wool slubbing is first
- 20 treated in a waterbath with a 2% aqueous solution of the particular softener. The wet slubbing is then whizzed to spin off excess softener solution. After air drying, the slubbing is (likewise in a waterbath) treated with a 1% aqueous solution of the antislip agent. After squeezing off and complete air drying, the slubbing is tested by the Aachen felting ball test (IWTO standard 20-69) for the quality of the antifelt finish. In addition, 4 people compare the hand of these wool slubbing samples
- 25 independently to determine the hand ranking.

Table (III) below contains the observed values for the felting ball diameter, the felt density and the hand ranking.

Table (III):

Example	9	10	11	12
Self-dispersing isocyanate	B2	B1	B2	B1
Softener	C1	C1	C2	C2
Antislip agent	D1	D1	D1	D1
Felting ball diameter [cm]	3.298	2.610	3.274	2.825
Felt density [g/cm <sup>3</sup> ]	0.053	0.107	0.054	0.085
Hand ranking	8	5	11	3

### Examples 13-16

- 5 (Order of treatment steps: a), b), c), d));  
Comparison of various antislip agents

- 10 Similarly to Examples 1-12, wool slubbing is first subjected to a corona treatment and then treated with an aqueous liquor containing 10 g/l of the water-dispersible isocyanate B2 and squeezed off on a lab pad-mangle to a wet pick-up of 80%. After rinsing out with water and air drying, the thusly pretreated wool slubbing is initially subjected in a waterbath and an exhaust process to a treatment with a 2% aqueous solution of the particular softener. The wet slubbing is then whizzed to spin off excess softener solution. After air drying, the slubbing is, likewise in a waterbath,
- 15 treated with an antislip agent (concentration of the antislip agent: 1% in water) in an exhaust process. After squeezing off, rinsing out and complete air drying, the slubbing is tested for the quality of its antifelt finish by the Aachen felting ball test (IWTO standard 20-69).
- 20 Table (IV) below shows the values observed for the felting ball diameter and the felt density.

Table (IV)

Example	13	14	15	16
Self-dispersing isocyanate	B2	B2	B2	B2
Softener	C1	C3	C1	C3
Antislip agent	D2	D2	D1	D1
Felting ball diameter [cm]	3.439	3.742	3.619	3.796
Felt density [g/cm <sup>3</sup> ]	0.047	0.037	0.040	0.035



Claims

1. Nonfelting wool, characterized in that the wool is
  - a) exposed to a plasma in a pretreatment,
  - b) optionally with an aqueous dispersion of self-dispersing isocyanates,
  - c) then with a softener and
  - d) optionally finally with an antislip agent.
2. Nonfelting wool, characterized in that the wool is
  - a) exposed to a plasma in a pretreatment,
  - b) with an aqueous dispersion of self-dispersing isocyanates,
  - c) then with a softener and
  - d) optionally finally with an antislip agent.
3. Nonfelting wool according to Claim 1 or 2, characterized in that the wool is raw wool after the raw wool scour, dyed or undyed wool slubbing, dyed or undyed wool yarn, knits or cloths.
4. Nonfelting wool according to Claim 1 or 2, characterized in that the self-dispersing isocyanates used in step b) have an isocyanate content of 1 - 25% by weight, reckoned as NCO (having a molecular weight of 42 g/mol), and are obtainable by reaction in any order of
  - I) organic polyisocyanates having an average NCO functionality of 1.8 - 4.2 with
  - II) polyalkylene oxide alcohols, amines and/or thiols of the formula 1
$$R^1R^2N-(CHX-CHY-O)_n-CHX-CHY-ZH \quad (1)$$

where

n is 3-70,

X and Y are hydrogen or methyl with the proviso that when one of X and Y is methyl the other must be hydrogen,

5 R<sup>1</sup> and R<sup>2</sup> are independently straight-chain or branched C<sub>1</sub>-C<sub>6</sub>-alkyl radicals or straight-chain or branched C<sub>1</sub>-C<sub>6</sub>-acyl radicals, with the proviso that if R<sup>1</sup> is a straight-chain or branched C<sub>1</sub>-C<sub>6</sub>-acyl radical, R<sup>2</sup> can also be hydrogen, and, furthermore, R<sup>1</sup> and R<sup>2</sup> may also combine to form a -(CH<sub>2</sub>)<sub>m</sub>- alkylene radical where m = 4, 5, 6 or 7, wherein one or two CH<sub>2</sub> groups can be replaced by O and/or NH and/or one or two CH<sub>2</sub> groups can be substituted by methyl, and

10 Z is O, S or NH,

15 and optionally

III) further NCO-reactive compounds containing anionic, cationic and/or potentially anionic or cationic groups,

20 and optionally

IV) further auxiliary and additive substances.

5. Nonfelting wool according to Claim 4, characterized in that the organic polyisocyanates I) are unmodified aliphatic, cycloaliphatic, araliphatic or aromatic isocyanates having an average NCO functionality of 1.8-4.2.

6. Nonfelting wool according to Claim 4, characterized in that the polyalkylene oxide alcohols, amines and/or thiols of the formula 1 contain on average 6-60 and preferably 7-20 alkylene oxide units per molecule.

7. Nonfelting wool according to Claim 6, characterized in that they are polyethylene oxide/propylene oxide alcohols, amines and/or thiols which preferably contain not less than 60 mol%, preferably not less than 70 mol%, of ethylene oxide units, based on the sum total of ethylene oxide and propylene oxide units.

8. Nonfelting wool according to Claim 4, characterized in that the NCO-reactive compounds III) are
- i) hydroxyl- or amino-functional compounds having tertiary amino groups,
  - 5 ii) hydroxyl- or amino-functional compounds having carboxyl or sulphonic acid groups,
  - iii) hydroxyl- or amino-functional compounds having carboxylate or sulphonate groups whose counterions are metal cations of the alkali metal or alkaline earth metal group or ammonium ions, or
  - 10 iv) hydroxyl- or amino-functional compounds having ammonium groups which are obtainable from the tertiary amino groups of the compounds i) by alkylation or protonation.
9. Nonfelting wool according to one or more of Claims 1 - 8, characterized in that the softeners used in step c) are fatty acid amides, ester quarts, quaternary fatty acid amides, betaines, fatty acid sarcosides, aminosilicones, polyethylene wax emulsions or silicone emulsions.
10. Nonfelting wool according to one or more of Claims 1 - 9, characterized in that the antislip agents used in step d) are anionic or cationic silica sols, blocked isocyanate resins, hydrophilicized isocyanate resins, polyacrylates or polyvinyl alcohols.
11. Process for the antifelt finishing of wool, characterized in that the wool is
- a) exposed to a plasma in a pretreatment,
  - b) optionally with an aqueous dispersion of self-dispersing isocyanates,
  - c) then with a softener and
  - d) optionally finally with an antislip agent.
12. Process for the antifelt finishing of wool according to Claim 11, characterized in that the aftertreatment b) of the wool material pretreated as per step a) is effected either batchwise in an exhaust process or continuously by dipping, roll application, padding, application of a mist or spray or backwasher application.

- Figure 1. The effect of the number of iterations on the accuracy of the proposed algorithm. The accuracy of the proposed algorithm increases with the number of iterations. The accuracy of the proposed algorithm is 100% when the number of iterations is 100.

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WOOL WITH ANTIFELT FINISH AND  
METHOD FOR PROVIDING AN ANTIFELT FINISH

ABSTRACT OF THE DISCLOSURE

The invention relates to nonfelting wool obtained by exposing wool to

- (a) a plasma in a pretreatment, followed by
- (b) optionally, an aqueous dispersion of self-dispersing isocyanates,
- (c) a softener, and
- (d) optionally, an antislip agent.

1001590 11229850

As a below named inventor, I hereby declare that:

My residence, post office address and citizenship are as stated below next to my name. I believe I am the original, first and sole inventor (if only one name is listed below) or an original, first and joint inventor (if plural names are listed below) of the subject matter which is claimed and for which a patent is sought on the invention entitled

**"WOOL WITH ANTIFELT FINISH AND METHOD FOR PROVIDING AN ANTIFELT FINISH"**

the specification of which is attached hereto,

or was filed on **December 6, 1999**

as a PCT Application Serial No. **PCT/EP99/09527**

I hereby state that I have reviewed and understand the contents of the above-identified specification, including the claims.

I acknowledge the duty to disclose information which is material to the patentability of this application in accordance with Title 37, Code of Federal Regulations, §1.56.

I hereby claim foreign priority benefits under Title 35, United States Code, §119 of any foreign application(s) for patent or inventor's certificate listed below and have also identified below any foreign application for patent or inventor's certificate having a filing date before that of the application on which priority is claimed:

Prior Foreign Application(s), the priority(ies) of which is/are to be claimed:

**198 58 734.1**  
(Number)

**Germany**  
(Country)

**December 18, 1998**  
(Month/Day/Year Filed)

I hereby claim the benefit under Title 35, United States Code, §120 of any United States application(s) listed below and, insofar as the subject matter of each of the claims of this application is not disclosed in the prior United States application in the manner provided by the first paragraph of Title 35, United States Code, §112, I acknowledge the duty to disclose the material information as defined in Title 37, Code of Federal Regulations, §1.56 which occurred between the filing date of the prior application and the national or PCT international filing date of this application:

(Application Serial No.)

(Filing Date)

(Status)

(patented, pending, abandoned)

(Application Serial No.)

(Filing Date)

(Status)

(patented, pending, abandoned)

I hereby declare that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code and that such willful false statements may jeopardize the validity of the application or any patent issued thereon.

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